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(54) ELECTRODE FOR CELL AND LITHIUM SECONDARY CELL EQUIPPED WITH THE ELECTRODE

(57)Abstract:

PURPOSE: To prevent each current collecting member from being formed into fine powder, and also prevent current collecting capacity from being degraded because of

cracks taken place, which are caused by the precipitation and dissolution of lithium at the time of charging/discharging by letting a negative electrode be composed of, metallic elements capable of making an alloy of lithium, and of metallic elements unable to make an alloy of lithium, and thereby extracting an output terminal at the negative electrode out of the metallic elements unable to make an alloy of lithium.

CONSTITUTION: In a cell equipped with a negative electrode 202, a positive electrode 203, electrolyte 204 and with a separator 205, the negative electrode 202 is made up of a member including metallic elements capable of making an alloy of lithium, and of a current collecting section 200 composed of metallic elements unable to make an alloy of lithium. By this constitution, even if charging/discharging are repeated, a current collecting member will never be degraded, and can thereby maintain its current collecting capacity. Therefore, an increase in charging voltage can be prevented at the time of charging at low amperage current, the occurrence of dendrite is thereby restrained, and its cycle life can be extended.

CLAIMS

[Claim(s)]

[Claim 1]In a lithium secondary battery which has a negative electrode, a separator, an anode, an electrolyte, or an electrolysis solution at least, A lithium secondary battery, wherein an output terminal by the side of a negative electrode is pulled out from a metal part which a negative electrode has as a component a metallic element which does not make at least a metallic element and lithium which make lithium and an alloy, and an alloy, is carried out, and does not make lithium and an alloy.

[Claim 2]The lithium secondary battery according to claim 1, wherein content of a metallic element which does not make lithium and an alloy from an anode, the surface which counters, and a portion connected with an output terminal in contact with an electrolysis solution of said negative electrode is high.

[Claim 3]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 2 to which said negative electrode is characterized by making a collecting member of metal which makes an alloy bind with a binder a member containing a metallic element from which lithium and an alloy of powder state are made to lithium.

[Claim 4]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 3, wherein said negative electrode comprises at least an alloy of lithium, metal which makes an alloy, and metal which does not make lithium and an alloy.

[Claim 5]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 4, wherein a member containing a metallic element which makes said lithium and an alloy differs in an etch rate and comprises selectively an alloy of two or more sorts of metal which can be etched.

[Claim 6]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 5 having the negative electrode of a metallic element which makes lithium and an alloy in said negative electrode, or a metallic element which does not make lithium and an alloy which etched any 1 way selectively at least, and had specific surface area raised.

[Claim 7]In contact with said electrolysis solution, a difference of one half and arithmetical-mean-deviation-of-profile Ra of maximum height Rmax (from the maximum mountain up to the deepest valley) of granularity of a conductor portion of an anode and a negative electrode surface which counters, A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 6 being 1/10 or less [of distance between a negative electrode surface and a positive electrode surface].

[Claim 8]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 7 characterized by 1+ (4 nRa/L) being 1.05 or more when setting arithmetical mean deviation of profile to Ra and setting the number of mountains of L and per the measurement length L to n for measurement length about granularity of a conductor portion of said negative electrode surface.

[Claim 9]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 8 providing a conductor layer whose pace of expansion in a room temperature is higher than metal which makes lithium and an alloy in a collecting section of said negative electrode.

[Claim 10]A metallic element which makes said lithium and an alloy Aluminum, magnesium, A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 6 being the elements more than a kind chosen from potassium, sodium, calcium, strontium, barium, silicon, germanium, tin, lead, indium, and zinc.

[Claim 11]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 6, wherein a collecting member which comprises a metallic element which does not make said lithium and an alloy is a member more than nickel, titanium, copper, silver, gold, platinum, iron, cobalt, chromium, tungsten, molybdenum, and a kind ** chosen.

[Claim 12]A conductor layer with a high pace of expansion arranged to a collecting section of said negative electrode Tin, a ****- bismuth alloy, A ****- lead alloy, a

zinc-aluminum alloy, a copper-zinc alloy, a cadmium zinc alloy, conductive ink to which conductor fines are made to bind with an organic high polymer material, the lithium secondary battery according to claim 9 comprising one or more kinds of conductors ** chosen.

[Claim 13]The lithium secondary battery according to claim 12, wherein organic high polymers in conductive ink used for a conductor layer with a high pace of expansion of said negative-electrode collecting section are a fluoro-resin which does not react to an electrolysis solution, polyolefine, silicon resin, and polymers that construct a bridge highly.

[Claim 14]The lithium secondary battery according to claim 1, wherein positive active material which constitutes said anode contains lithium elements.

[Claim 15]A lithium secondary battery given in any 1 paragraph of claims 1 thru/or 8, wherein a lithium metal which deposited by charge although said negative electrode surface could penetrate a lithium ion which does not dissolve in an electrolysis solution is covered with an insulator film or semiconductor membrane which is not penetrated.

[Claim 16]An electrode for cells characterized by pulling out an output terminal from a metal part which has as a component a metallic element which does not make at least a metallic element and lithium which make lithium and an alloy, and an alloy, and does not make lithium and an alloy.

[Claim 17]The electrode for cells according to claim 16, wherein content of a metallic element which does not make lithium and an alloy from an anode, the surface which counters, and a portion connected with an output terminal in contact with an electrolysis solution of said negative electrode is high.

[Claim 18]The electrode for cells according to claim 16 or 17 to which said negative electrode is characterized by making a collecting member of metal which makes an alloy bind with a binder a member containing a metallic element from which lithium and an alloy of powder state are made to lithium.

[Claim 19]The electrode for cells according to claim 16 to 18, wherein said negative electrode comprises at least an alloy of lithium, metal which makes an alloy, and metal which does not make lithium and an alloy.

[Claim 20]The electrode for cells according to claim 16 to 19, wherein a member containing a metallic element which makes said lithium and an alloy differs in an etch rate and comprises selectively an alloy of two or more sorts of metal which can be etched.

[Claim 21]The electrode for cells according to claim 16 to 20 having the negative electrode of a metallic element which makes lithium and an alloy in said negative electrode, or a metallic element which does not make lithium and an alloy which etched any 1 way selectively at least, and had specific surface area raised.

[Claim 22]The electrode for cells according to claim 16 to 21 to which a difference of one half and arithmetical-mean-deviation-of-profile Ra of maximum height Rmax (from

the maximum mountain up to the deepest valley) of granularity of a conductor portion of an anode and a negative electrode surface which counters is characterized by being 1/10 or less [of distance between a negative electrode surface and a positive electrode surface] in contact with said electrolysis solution.

[Claim 23]The electrode for cells according to claim 16 to 22 characterized by 1+ (4 nRa/L) being 1.05 or more when setting arithmetical mean deviation of profile to Ra and setting the number of mountains of L and per the measurement length L to n for measurement length about granularity of a conductor portion of said negative electrode surface.

[Claim 24]The electrode for cells according to claim 16 to 23 providing a conductor layer whose pace of expansion in a room temperature is higher than metal which makes lithium and an alloy in a collecting section of said negative electrode.

[Claim 25]A metallic element which makes said lithium and an alloy Aluminum, magnesium, Potassium, sodium, calcium, strontium, barium, silicon, germanium, tin, lead, indium, the electrode for cells according to claim 16 to 21 being the elements more than a kind chosen from zinc.

[Claim 26]The electrode for cells according to claim 16 to 21, wherein a collecting member which comprises a metallic element which does not make said lithium and an alloy is a member more than nickel, titanium, copper, silver, gold, platinum, iron, cobalt, chromium, tungsten, molybdenum, and a kind ** chosen.

[Claim 27]A conductor layer with a high pace of expansion arranged to a collecting section of said negative electrode Tin, a ****- bismuth alloy, The electrode for cells according to claim 24 comprising a ****- lead alloy, a zinc-aluminum alloy, a copper-zinc alloy, a cadmium zinc alloy, conductive ink to which conductor fines are made to bind with an organic high polymer material, and one or more kinds of conductors ** chosen.

[Claim 28]The electrode for cells according to claim 27, wherein organic high polymers in conductive ink used for a conductor layer with a high pace of expansion of said negative-electrode collecting section are a fluoro-resin which does not react to an electrolysis solution, polyolefine, silicon resin, and polymers that construct a bridge highly.

[Claim 29]The electrode for cells according to claim 6, wherein positive active material which constitutes said anode contains lithium elements.

[Claim 30]The electrode for cells according to claim 16 to 23, wherein a lithium metal which deposited by charge although said negative electrode surface could penetrate a lithium ion which does not dissolve in an electrolysis solution is covered with an insulator film or semiconductor membrane which is not penetrated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the lithium secondary battery which generating of the dendrite (resin-like projection) of the lithium by which it is especially generated by repetition of charge and discharge can be suppressed about the lithium secondary battery which uses lithium for a negative electrode, and can suppress the fall of current collection ability.

[0002]

[Description of the Prior Art]A possibility that global warming will arise these days in the greenhouse effect by the increase in CO_2 contained in the atmosphere is pointed out. Although the thermal energy produced by a thermal power plant burning a fossil fuel etc. is transformed into electrical energy, since CO_2 is discharged with combustion, construction of a new thermal power plant is becoming difficult. Then, performing what is called load leveling that stores the night power which is surplus electric power as effective use of a dynamo in the rechargeable battery installed in an ordinary home, and equalizes load is being advocated. The demand of development of the rechargeable battery of high energy density by a light weight for the electromobile which does not discharge the substance said to be involved in the air pollution containing COx, NOx, SOx, hydrocarbon, etc., The demand of the development of a small, lightweight, and highly efficient rechargeable battery used for the power supply of portable devices, such as a book mold personal computer, a word processor, a video camera, and a cellular phone, is increasing increasingly.

[0003]

[Problem(s) to be Solved by the Invention]Development of the rocking chair type lithium ion battery which used for positive active material what introduced the lithium ion into the intercalation compound as one of the rechargeable batteries of the above-mentioned high performance, and used carbon for negative electrode active material progresses, and a part is being put in practical use. However, the lithium ion battery which can be gained now has not fully attained the high energy density which is the original feature of a lithium cell which uses metal lithium for negative electrode active material. The lithium battery of the high capacity which uses a lithium metal with a high attention degree for a negative electrode as a high-energy-density rechargeable battery cannot say that sufficient utilization is made. As for a lithium secondary battery, arborescence lithium may deposit on a negative electrode at the time of charge. This phenomenon may cause a short circuit and self-discharge. generating one of the reasons sufficient utilization of the lithium battery (rechargeable battery) of high capacity is not made, by repetition of charge and discharge -- simplistic -- it is because it has not succeeded in suppressing generating of the dendrite of lithium which becomes a main

cause. Since the energy which a cell has will be consumed in the portion for a short time if the dendrite of lithium grows and a negative electrode and an anode short-circuit, a cell may generate heat, or the solvent of an electrolysis solution decomposes with heat etc., gas is generated, and the internal pressure in a cell may high-feel easy. Anyway, growth of a dendrite leads to the damage and life decline of a cell by a short circuit easily.

[0004]In order to stop the reactivity of lithium and to suppress generating of a dendrite, the method of using lithium alloys, such as lithium aluminum, for a negative electrode is also tried. However, even if it can control generating of a dendrite, it is high energy density and the actual condition is that what has a cycle life long enough has not resulted in utilization.

[0005]As an example which uses a lithium alloy for a negative electrode, it is shown, for example in JP,63-13264,A, JP,5-47381,A, JP,5-190171,A, etc. However, even if it used the lithium alloy for the negative electrode, while repeating charge and discharge, the negative electrode repeated expansion and contraction, and there was a case where a crack etc. arose in a negative electrode and it became impossible to maintain sufficient current collection nature.

[0006]The negative electrode which used as the base the mixed sintered body of fibrous aluminum, and lithium and the metal fiber which is not alloyed is shown in JP,63-114057,A. However, there was a case where the fall of the associative strength of lithium and the metal fiber which is not alloyed and generating of the crack in an interface with that arose, and it became impossible to maintain sufficient current collection nature by expansion of fibrous aluminum accompanying charge and discharge and contraction in this case.

[0007]The metal powder which cannot generate an intermetallic compound with a lithium metal easily on the surface of the substrate which becomes JP,5-234585,A from a lithium metal is made to adhere uniformly, the deposit of a dendrite lessens and the cell which raises a cycle life is highly shown in charging efficiency. However, as a result of producing omission of the powder which the lithium metal which is a substrate too repeated expansion and contraction by charge and discharge, and was made to adhere, and the crack of a substrate, there is a case where maintenance of sufficient current collection nature of a negative electrode and control of a deposit of a dendrite fully become impossible as mentioned above.

[0008]JOURNAL OF APPLIED ELECTROCHEMISTRY 22 and 620-627 -- **** (1992) -- the report of the lithium secondary battery which used for the negative electrode the aluminium foil which carried out the etching process of the surface is carried out. However, if a charging and discharging cycle is repeated to a practical use region, as a result of aluminium foil's repeating expansion contraction by repetition of charge and discharge, a crack goes into aluminium foil and growth of a dendrite takes place with the fall of current collection nature. Therefore, the cell of the long cycle life

in a practical use level is not obtained in this case, either. Thus, an energy density is high and the actual condition has a problem which should still be solved actually to waiting eagerly for the appearance of the long negative electrode of a cycle life, and a lithium secondary battery.

[0009](The purpose of an invention) This invention can solve an above-mentioned problem and an object of this invention is to provide the lithium secondary battery of high energy density by a long cycle life.

[0010]An object of this invention is to provide the lithium secondary battery which has the electrode for cells and this electrode which have the negative electrode structure which can suppress the fall of the current collection ability by the pulverization by the deposit dissolution of lithium and crack initiation at the time of charge and discharge.

[0011]

[Means for Solving the Problem and its Function]The above-mentioned problem is solved, an electrode for cells of this invention which attains the above-mentioned purpose has as a component a metallic element which does not make at least a metallic element and lithium which make lithium and an alloy, and an alloy, and an output terminal is pulled out from a metal part which does not make lithium and an alloy.

[0012]In a lithium secondary battery with which a lithium secondary battery of this invention has a negative electrode, a separator, an anode, an electrolyte, or an electrolysis solution at least, An output terminal by the side of a negative electrode is pulled out from a metal part from which a negative electrode has as a component a metallic element which does not make at least a metallic element and lithium which make lithium and an alloy, and an alloy, and does not make lithium and an alloy.

[0013]That this invention person should solve the above-mentioned problem, as a result of repeating research wholeheartedly, by using appropriately a negative electrode which lithium, metal to alloy, lithium, and metal which is not alloyed composite-ized, Generating of a dendrite of lithium stops and it is based on having found out that a long lasting lithium secondary battery was obtained.

[0014]Namely, in a rechargeable battery with which the above-mentioned problem has a negative electrode, a separator, an anode, an electrolyte or an electrolysis solution, and a cell case at least, It comprises a metallic element from which a negative electrode does not make at least a metallic element and lithium which make lithium and an alloy, and an alloy, and can solve with a lithium secondary battery by which an output terminal by the side of a negative electrode is pulled out from metal which does not make lithium and an alloy. Thus, by arranging metal which does not make lithium and an alloy to a negative-electrode collecting section, a fall of current collection ability by pulverization and crack initiation by the deposit dissolution of lithium at the time of charge and discharge can be suppressed.

[0015]A negative electrode of this invention is a collecting section connected with an anode, the surface which counters, and an output terminal in contact with an electrolysis

solution, and that of making high content of a metallic element which does not make lithium and an alloy is preferred.

[0016]In a negative electrode which consists of an element which makes lithium and an alloy, at the time of charge, lithium deposits, and alloys and expands, at the time of discharge, lithium is emitted into an electrolysis solution, and contracts, and pulverization happens. This pulverization happens most actively in a negative electrode surface where an element which makes reactant high lithium and an alloy exists. In a part where pulverization occurred, conductivity will fall and current collection ability will fall remarkably. Therefore, by raising an anode and content of a metallic element which does not make lithium and an alloy on the current-carrying-part surface which counters in contact with an electrolysis solution of a negative electrode, since conductivity is maintained via metal which does not make lithium and an alloy at the time of pulverization, either, a fall of current collection ability can be controlled more.

[0017]With a binder, a collecting member of metal which does not make an alloy is made to bind to lithium, and a member of powder state containing a metallic element which makes lithium and an alloy for a negative electrode of this invention may be calcinated formation or after that, and may be formed.

[0018]Fatigue breaking which occurs from a repetition of contraction by elution of lithium at the time of expansion by alloying with lithium at the time of charge and discharge can be controlled by considering it as such a negative electrode. By adopting a granular material, specific surface area of a negative electrode can be raised, a touch area with an electrolysis solution can increase, and diffusion of a lithium ion to a negative electrode can be made easy. By processing etching etc., specific surface area can be increased further, dendritic growth of lithium can be stopped, and efficiency of charge and discharge can be raised. Control of concentration of a metallic element which does not make a metallic element and lithium which make lithium and an alloy in thickness of a negative electrode and a negative electrode, and an alloy becomes easy.

[0019]a case where fabricate a member containing a metallic element which makes lithium and an alloy, and it is not sintered with a binder to a negative electrode -- an electric conduction adjuvant of carbon powder or a metal powder -- about 1-25wt% -- it is necessary to mix and to improve the current collection nature of the granular materials of a member containing a metallic element which is easy to make lithium and an alloy Since a small thing of bulk density tends to hold an electrolysis solution as the above-mentioned electric conduction adjuvant, it is easy to lower impedance of an electrode. Bulk density of a more desirable electric conduction auxiliary material is 0.1 or less.

[0020]If particle diameter of an electric conduction auxiliary material is fine, the finer one is good, but in order to raise packing density and to improve current collection nature, it is good to combine an electric conduction adjuvant of shape, such as a globular shape, a needle, and the shape of a flake (the shape of a folia).

[0021]When making it sinter, as a material used for a binder, it is inorganic materials or organic materials which do not emit corrosive gas as much as possible, such as halogen, under an elevated temperature, and, in the case of organic materials, polymers which are easy to carbonize are preferred. Sintering atmosphere has the preferred bottom of decompression or inactive gas, and reducing gas.

[0022]An alloy of lithium, metal which makes an alloy, and metal which does not make lithium and an alloy may be used for a negative electrode of this invention further at least further again. It becomes possible to be able to raise current collection ability and to develop a charge-and-discharge cycle life further to an inside of a negative electrode, by this.

[0023]It is good also as what etch rates differ and comprises selectively an alloy of two or more sorts of metal which can be etched in a member containing a metallic element which makes lithium and an alloy of a negative electrode. By performing an etching process to this negative electrode further, specific surface area of a negative electrode can be increased by leaps and bounds.

[0024]It is also preferred to etch selectively a metallic element which makes lithium and an alloy in a negative electrode of this invention, or a metallic element which does not make lithium and an alloy, and to raise specific surface area of a negative electrode. By raising specific surface area of a negative electrode, the reactivity of a negative electrode surface can be improved, current density of parenchyma can be lowered, a charge-and-discharge reaction can be made smooth, and, as a result, a cycle life can be developed.

[0025]By a height, when a height exists in a negative electrode surface which established uneven shape and raised specific surface area, since an electric field concentrates at the time of charge and current density increases, dendritic growth of lithium happens easily and it is easy to grow into a short circuit cause.

[0026]Then, it is desirable to make or less [of distance between a negative electrode surface and a positive electrode surface] into 1/10 a difference of one half and arithmetical mean deviation of profile of maximum height Rmax (from the maximum mountain up to the deepest valley) of granularity of a conductor portion of a negative electrode surface which counter with an anode in contact with an electrolysis solution.

[0027]It is preferred that a ratio of conductivity of a trough to conductivity of a height of a negative electrode surface uses ten or less. Namely, a difference of one half and arithmetical mean deviation of profile of height Rmax of a height of a negative electrode surface, Since line of electric force is not concentrated on a height and field intensity does not become large when larger than 1/10 of distance between a negative electrode surface and a positive electrode surface and electrical resistance of a height is larger than electrical resistance of a flat part, lithium does not carry out dendritic growth to a height at the time of charge.

[0028]When conductivity of a conductor portion of a negative electrode surface is

uniform or substantially uniform, As a negative electrode surface before assembling a cell with a stylus method was shown in drawing 6, maximum height Rmax and arithmetical-mean-deviation-of-profile Ra were measured, a cycle life of various negative electrodes was measured on conditions from which dendritic growth of lithium which formed a cell using this negative electrode after that, and raised charge voltages happens easily, and correlation was taken. As a result, as shown in drawing 7, a certain amount of correlation was able to be taken between a difference of one half and arithmetical-mean-deviation-of-profile Ra of granularity (from maximum mountain up to deepest valley) maximum height Rmax of a conductor portion of an anode and a negative electrode surface which counters, and a cycle life of a negative electrode. That is, it became clear that a case where a difference of one half and arithmetical mean deviation of profile of what lengthened minimum height from the maximum height of granularity of a conductor portion of a negative electrode surface uses 1/10 or less [of distance between a negative electrode surface and a positive electrode surface], and a cycle life became longer.

[0029]When setting arithmetical mean deviation of profile to Ra and setting the number of mountains of L and per the measurement length L to n for measurement length about granularity of a conductor portion of a negative electrode surface of this invention, it is preferred that 1+ (4 nRa/L) uses 1.05 or more.

[0030]Examination showed wholeheartedly that surface reactivity was improved, and the increase of specific surface area and substantial current density fell, and a charge-and-discharge cycle life could be prolonged by damaging a negative electrode surface by an etching process etc. If surface roughness of a negative electrode before charge and discharge and correlation of a cycle life are taken, data like drawing 8 will be obtained, When setting arithmetical mean deviation of profile to Ra and setting the number of mountains of L and per the measurement length L to n for measurement length, when 1+ (4 nRa/L) uses 1.2 or more more preferably 1.1 or more 1.05 or more showed that a cycle life was extended more than twice. Aluminum is used for an element which makes lithium and an alloy of a negative electrode of this invention from drawing 8, After damaging the surface in various etching processes, to positive active material a lithium nickel oxide, It is the result of assembling a cell using an electrolysis solution which dissolved lithium borofluoride in ethylene carbonate dimethyl carbonate (EC-DMC) or a propylene carbonate diethyl carbonate (PC-DEC) mixed solvent to an electrolysis solution, and measuring a charge-and-discharge cycle life.

[0031]In this invention, a conductor layer whose pace of expansion in a room temperature is higher than metal which makes lithium and an alloy may be provided in a collecting section of a negative electrode. When lithium aluminum alloy foil or aluminium foil is used for a negative electrode, by repetition of charge and discharge, pulverization may occur in a negative electrode surface, a crack may arise, and current collection may become impossible eventually. This is guessed that expansion

contraction of a negative electrode at the time of charge and discharge is the main cause. However, by providing a conductor layer with a high pace of expansion in a room temperature in a collecting section, a crack of a collecting section by expansion contraction of a negative electrode is suppressed further, and reservation of current collection ability is attained.

[0032]Positive active material which constitutes an anode may be made to contain lithium elements. Alloying with lithium in a negative electrode and an element which makes an alloy will not be performed without this by deposit of lithium at the time of charge. A manufacturing process is simplified, in order produce an alloy of lithium and not to prepare it beforehand from the time of an assembly of a cell. Since there is little expansion contraction of an anode by which it is accompanied at the time of discharge charge since discharge insertion of the lithium which existed in charge and discharge in an anode beforehand is carried out and omission of positive active material from a charge collector do not arise, a cycle life will be extended.

[0033]Although a lithium ion can be penetrated, a lithium metal which deposited at the time of charge may cover a negative electrode surface with an insulator film or semiconductor membrane which is not penetrated. It prevents generating a reactant lithium which deposits at the time of charge becomes difficult to contact an electrolysis solution directly, activity lithium reacts, and it becomes impossible to contribute to discharge by this, and it becomes possible to prolong a charge-and-discharge cycle life. Subsequently, when a negative electrode is formed from a granular material, surface coating of a negative electrode is effective in suppressing omission of a granular material.

[0034]Hereafter, a lithium secondary battery of this invention is explained, referring to drawings.

[0035]A cross section of an example of a negative electrode which can be used conveniently for a lithium secondary battery of this invention, respectively was shown in drawing 2 and drawing 3. Although not illustrated, when it actually constitutes a cell, in drawing 2 and drawing 3, a separator and an anode are countered and provided in the upper part of a drawing top negative electrode.

[0036]A negative electrode shown in drawing 2 (a) is a case of a negative electrode which comprised the collecting section 101 which comprises a metallic element which does not make the member 102 and lithium containing a metallic element which does not make lithium and an alloy, and an alloy. At the time of charge, a lithium ion in an electrolysis solution alloys a negative electrode shown in drawing 2 (a) with lithium and the member 102 containing a metallic element which makes an alloy, and it deposits and expands. Subsequently, in discharge, from the member 102 containing a metallic element which makes lithium and an alloy, a lithium ion is emitted into an electrolysis solution and contracts. Although pulverization and a crack of the member 102 which contain a metallic element which makes lithium and an alloy by expansion contraction

by this charge and discharge occur, Since the layer 101 of a metallic element which does not make lithium and an alloy is formed in a collecting section, omission into an electrolysis solution of the member 102 containing lithium into which a fall of current collection ability was small, and carried out pulverization, and a crack went, and a metallic element which makes an alloy will be suppressed.

[0037]A negative electrode shown in drawing 2 (b) is a case where the metallic element 106 which does not make lithium and an alloy on the surface of a negative electrode of composition of drawing 2 (a) has been arranged. In this case, from a case of a negative electrode of composition of being shown in drawing 2 (a), by lithium further arranged to a negative electrode surface, and the metallic element 106 which does not make an alloy, a fall of current collection ability of a plane direction can be suppressed, and promotion of pulverization can be suppressed in a negative electrode surface where pulverization occurs easiliest.

[0038]The collecting member 101 which comprises a metallic element which mixes the electric conduction adjuvant 104 with lithium to the powder state member 103 containing a metallic element which makes an alloy, and does not make lithium and an alloy from the binder 105 is made to bind a negative electrode shown in drawing 2 (c), and it forms an active layer. By using a granular material for a member containing a metallic element which makes lithium and an alloy from the beginning not using a massive thing, stress accompanying expansion contraction generated at the time of charge and discharge can be eased, fatigue breaking can be prevented, and a charge-and-discharge cycle life can be prolonged further. A touch area with an electrolysis solution can be increased and a reaction at the time of charge and discharge can be smoothly carried out more to homogeneity.

[0039]A negative electrode shown in drawing 2 (c') forms the same active layer as a negative electrode shown in drawing 2 (c) in both sides of the collecting member 101 which comprises a metallic element which does not make lithium and an alloy, a vertical section is countered in this case, and a separator and an anode may be arranged. Especially an electrode configuration of a negative electrode shown in drawing 2 (c') which carries out a collecting section in common and provides an active layer in both sides is more effective in a spiral shape cylindrical shape cell or a square-shaped cell of lamination type electrode formation in respect of an increase in reduction of a manufacturing process and material, and electric capacity per unit volume.

[0040]A negative electrode shown in drawing 3 (d) is a negative electrode which formed the conductor layer 107 with a high pace of expansion between the collecting sections 101 which comprise a metallic element which does not make the member 102 and lithium containing a metallic element which makes lithium and an alloy of a negative electrode of composition of drawing 1 (a), and an alloy. The conductor layer 107 with a high pace of expansion can follow in footsteps of expansion contraction, and the member 102 containing a metallic element which makes lithium and an alloy can

suppress a fall of current collection ability more, also when a crack occurs in expansion contraction by a charging and discharging cycle. Omission into an electrolysis solution of the member 102 containing a metallic element which makes lithium and an alloy can also be prevented.

[0041]A negative electrode shown in drawing 3 (e) is a negative electrode which has arranged the metallic element 106 which does not make lithium and an alloy at the member 102 surface and a rear face containing a metallic element which makes lithium and an alloy, and covered a collecting section with the conductor layer 107 with a high pace of expansion. Omission into a problem in a negative electrode surface and a fall of current collection ability of a collecting section by repetition of a charging and discharging cycle, and an electrolysis solution of the member 102 containing a metallic element which makes lithium and an alloy can also be prevented.

[0042]A negative electrode shown in drawing 3 (f) is the example which covered a collecting section of a negative electrode of composition of being shown in drawing 3 (a) with the conductor layer 107 with a high pace of expansion. A fall of current collection ability of a collecting section can be suppressed, and omission into an electrolysis solution of the member 102 containing a metallic element which makes lithium and an alloy can also be prevented.

[0043]A negative electrode shown in drawing 3 (g) adopts as a negative electrode the alloy 108 of a metallic element which does not make a metallic element and lithium which make lithium and an alloy, and an alloy. It can apply, also when a member which contains a metallic element which makes lithium and an alloy like [in the case of a negative electrode shown in drawing 3 (c)] is a granular material. By using the alloy 108 of a metallic element which does not make a metallic element and lithium which make lithium and an alloy, and an alloy, it becomes possible to prevent metaled pulverization and a crack development which arrange a metallic element which does not make lithium and an alloy, can hold current collection ability, and make lithium and an alloy to an internal detailed part. Here, as for a rate of a metallic element which makes the above-mentioned lithium and an alloy, it is desirable that it is not less than 50% so that there may be no utilization efficiency lowering of lithium. Selective etching is possible if rates of an etching ratio of a metallic element which does not make a metallic element and lithium which make lithium and an alloy, and an alloy differ, By carrying out etching removal of a part of metallic element which does not make a metallic element or lithium which makes lithium and an alloy, and an alloy, it becomes possible to obtain very high specific surface area.

[0044]A rechargeable battery as shown in drawing 1 combining an anode, a separator, and an electrolyte using a negative electrode as been at drawing 2 and drawing 3 and shown can be formed. A collecting section which comprises a metallic element from which 200 does not mainly make lithium and an alloy in drawing 1, a layer which comprises a member containing a metallic element from which 201 mainly makes

lithium and an alloy, and 202 -- a negative electrode and 203 -- an anode and 204 -- an electrolyte (electrolysis solution) and 205 -- a separator and 206 -- a negative pole terminal and 207 -- a positive pole terminal and 208 -- a cell case -- it comes out. It cannot be overemphasized that composition of the negative electrode 202 is transposed to composition of a negative electrode shown in drawing 2 and drawing 3, respectively, respectively.

[0045]Since a negative electrode of this invention comprises a collecting section which comprises a metallic element which does not make a member and lithium containing a metallic element which makes lithium and an alloy, and an alloy, Even if it repeats charge and discharge, a collecting member which comprises a metallic element which does not make lithium and an alloy does not deteriorate, current collection ability can be maintained, a rise of charge voltages at the time of constant current charge is suppressed, dendrite generating can be controlled, and it becomes possible to develop a cycle life as a result.

[0046](Negative electrode) A negative electrode of this invention has as a component a metallic element which does not make at least a metallic element and lithium which make lithium and an alloy, and an alloy, and an output terminal by the side of a negative electrode is pulled out from a collecting section which has arranged metal which does not make lithium and an alloy.

[0047]. [whether a metallic element which does not make lithium and an alloy to a collecting section of a member of a board which contains a metallic element which makes lithium and an alloy as a actual negative electrode, or foil form is arranged, and] A thing in which a layer which consists of powder containing a metallic element which makes lithium and an alloy was formed on a collecting member of metal which does not make lithium and an alloy is used. A metallic element which does not make lithium and an alloy is arranged on an anode of the above-mentioned negative electrode, and the surface which counters, and current collection ability is raised to it.

[0048]It is usable also in an alloy of the above-mentioned lithium, a metallic element which makes lithium and an alloy at a member containing a metallic element which makes an alloy, and lithium and a metallic element which does not make an alloy.

[0049]A collecting section of the above-mentioned negative electrode is covered with a conductive layer with a high pace of expansion, and fatigue breaking accompanied by expansion contraction by repetition of charge and discharge is protected from metal which makes lithium and an alloy from a room temperature.

[0050]<Arrangement of a metallic element which does not make lithium and an alloy> It processes to this by using as a negative-electrode substrate a member which consists of a metallic element which makes lithium and an alloy first, and an example of how to arrange a metallic element which does not make lithium and an alloy is explained below. The above-mentioned lithium, an anode of a negative electrode of a metallic element which does not make an alloy, the surface that counters, and a method of arranging to a

collecting section have the following methods.

[0051]When an ionization tendency of a metallic element which makes lithium and an alloy is higher than a metallic element which does not make lithium and an alloy, By dipping a member which consists of a metallic element which makes lithium and an alloy in a solution of a salt of a metallic element which does not make lithium and an alloy, a part of metallic element which makes lithium and an alloy can be replaced by a metallic element which does not make lithium and an alloy. The amount of substitution is controllable by concentration of a salt in time to dip in a solution, and a solution, temperature of a solution, etc. That is, if time to dip in a solution is lengthened, the amount of substitution will increase, and if concentration of a salt in a solution is raised or temperature of a solution is raised, speed of a substitution reaction will be increased.

[0052]A layer which contains a metallic element which does not make lithium and an alloy as other configuration methods, Electrolytic plating, plating unelectrolyzed (chemicals), laser plating, sputtering, A method of making it laminate on a substrate by resistance heating vacuum evaporation, electron beam evaporation, ionized cluster beam vacuum evaporation, the heat CVD (Chemical VaporDeposition), the decompression CVD, plasma CVD, laser CVD, etc. can be used. The coating technique containing a metallic element which does not make lithium and alloys in a method, such as screen-stencil, of ink or a paste can also be used.

[0053]A substrate which changes from a metallic element which does not make lithium and an alloy to other methods is used as it is as a charge collector, The technique of sputtering, resistance heating vacuum evaporation, electron beam evaporation, ionized cluster beam vacuum evaporation, the heat CVD, the decompression CVD, plasma CVD, screen-stencil, etc. coating a layer which comprises a metallic element which makes lithium and an alloy on it, and forming it by a method is also employable. As shape of a substrate which comprises a metallic element which does not make lithium and an alloy, various shape, such as a board, foil, a punching metal, an expanded metal, and mesh state, can be used.

[0054]<Metallic element which does not make a metallic element and lithium which make lithium and an alloy, and an alloy> as a metallic element which makes lithium and an alloy, Aluminum, magnesium, potassium, sodium, calcium, strontium, barium, silicon, germanium, tin, lead, indium, zinc, etc. can be used, and aluminum, magnesium, calcium, and lead are especially preferred.

[0055]As a metallic element which does not make lithium and an alloy, nickel, titanium, copper, silver, gold, platinum, iron, cobalt, chromium, tungsten, molybdenum, etc. can be used, and nickel, titanium, copper, platinum, and iron ** is especially preferred. As a collecting member, an alloy which comprises the above-mentioned element besides a single metal of the above-mentioned element is employable. A stainless steel is also a material desirable as a collecting member which does not make lithium and an alloy.

[0056]<Negative electrode which comprises powder containing a metallic element

which makes lithium and an alloy> as a concrete method of forming on a collecting member, a layer which comprises powder containing a metallic element which makes the above-mentioned lithium and an alloy, Mix resin or low melting glass as a binder to powder containing a metallic element which makes lithium and an alloy, or powder of an alloy of a metallic element which does not make a metallic element and lithium which make lithium and an alloy, and an alloy, and an organic solvent etc. are added to it, After applying a paste which adjusted viscosity on a collecting member of metal which does not make lithium and an alloy, a method of drying, or sintering and forming is employable.

[0057]When using an organic high polymer as the above-mentioned binder, A stable thing is preferred to an electrolysis solution, for example, can mention polytetrafluoroethylene, poly fluoridation kinky thread NIDEN, polyethylene, polypropylene, an ethylene propylene copolymer, an ethylene-propylene-diene terpolymer, silicon resin, etc. to it. Besides these, polymers ** which constructs a bridge highly is mentioned as a desirable material. When adopting an organic high polymer as a binder, although there are few omission of an active material, since it is low compared with a case where current collection ability is metal, also by expansion contraction by charge and discharge, It is preferred to add carbon powder and fine-metallic-powder objects, such as carbon black, Ketchen black, acetylene black, and black lead, and to improve current collection ability as an electric conduction adjuvant. In large shape in parallel where it is perpendicularly thin, to black lead as an electric conduction auxiliary material especially in a crystal face. Since current collection ability will be raised since conductivity is high if bulk density uses 0.1 or less flake-like black lead, and the amount of maintenance of an electrolysis solution can also be raised, impedance of a negative electrode formed from powder can be made low.

[0058]Although low melting glass can also be used as the above-mentioned binder, compared with a case where resin is used, expansion contraction or a mechanical strength depended for bending becomes weak in this case.

[0059]The above-mentioned collecting member requires at least that the surface should be the conducting material covered with a metallic element which does not make lithium and an alloy. As shape of a collecting member, various kinds of shape, such as tabular, foil form, mesh state, the shape of sponge, fibrous, a punching metal, and an expanded metal, is employable. As a material of the above-mentioned collecting member, nickel, copper, titanium, aluminum, silver, gold, platinum, iron, a stainless steel, etc. are mentioned.

[0060]<Covering of a collecting section in a conductor layer with a high pace of expansion> as a concrete formation method of a conductor layer with a high pace of expansion, Methods, such as sputtering, resistance heating vacuum evaporation, electron beam evaporation, ionized cluster beam vacuum evaporation, the heat CVD, the decompression CVD, plasma CVD, laser CVD, electrolytic plating, plating

unelectrolyzed (chemicals), and laser plating, can be used. A coating method represented by screen-stencil of ink containing a conductor with a high pace of expansion, etc. can also be used.

[0061]As an example of a conductor layer with a high pace of expansion arranged to a collecting section of the above-mentioned negative electrode, A comprising-tin, ****- bismuth alloy, ****- lead alloy, zinc-aluminum alloy, copper-zinc alloy, cadmium zinc alloy, conductive ink [to which conductor fines are made to bind with an organic high polymer material], and one or more kinds of conductors ** chosen conductor layer is mentioned. Depending on the case, it is usable also in gold, silver, aluminum, and those alloys.

[0062]It is preferred that they are a fluoro-resin, polyolefine, silicon resin, and polymers that construct a bridge highly which do not react to an electrolysis solution as an organic high polymer in conductive ink used for a conductor layer with a high pace of expansion of the above-mentioned negative-electrode collecting section. It is desirable for the above-mentioned organic high polymer glass transition temperature to be below minimum temperature of actual use temperature, for example, it is more preferred that it is less than minus 30 **.

[0063]<Etching of a negative electrode> Specific surface area of a negative electrode can be increased by etching the surface of a negative electrode of this invention which comprises a collecting member which comprises a metallic element which does not make a member and lithium containing a metallic element which makes lithium and an alloy, and an alloy.

[0064]As an etching method, techniques, such as chemical etching, electrochemical etching, and plasma etching, are employable.

[0065]Chemical etching is made to react to acid or alkali, and is etched. There is the following as an example.

[0066]As an etching reagent of aluminum which is a metallic element which makes lithium and an alloy, phosphoric acid, sulfuric acid, chloride, nitric acid, acetic acid, fluoric acid, a potassium hydrate, sodium hydroxide, lithium hydroxide, these mixed solutions, etc. are used.

[0067]As an etching reagent in case a metallic element which makes lithium and an alloy is magnesium, nitric acid, sulfuric acid, chloride, alkaline aqueous solutions that mixed ammonium salt, these mixed solutions, etc. are used.

[0068]Dilute acid, such as nitric acid, is used as an etching reagent in case a metallic element which does not make lithium and an alloy is nickel.

[0069]an etching reagent in case a metallic element which does not make lithium and an alloy is copper -- carrying out -- organic acid, such as sulfuric acid, chloride, nitric acid, and acetic acid, a cupric chloride solution, a ferric chloride solution, an ammonia solution, etc. can be used.

[0070]an etching reagent in case a metallic element which does not make lithium and an

alloy is titanium -- carrying out -- fluoric acid, phosphoric acid, etc. can be used.

[0071]It is preferred for etch rate ratios of a metallic element and lithium which make lithium and an alloy, and a metallic element which does not make an alloy to differ in the case of chemical etching, and to use for it an etching reagent in which selective etching is possible.

[0072]Electrochemical etching impresses an electric field between counter electrodes, and is made electrochemically eluted as a metal ion in an electrolysis solution.

[0073]As an electrolysis solution of aluminum which is a metallic element which makes lithium and an alloy, a mixed solution of phosphoric acid, sulfuric acid, and chromic acid, etc. are used.

[0074]an etching reagent in case a metallic element which does not make lithium and an alloy is copper -- carrying out -- a phosphoric acid solution etc. can be used.

[0075]Plasma etching is the method of plasma-izing gas for etching, making reactant ion and a radical react, and etching. As etching gas of a raw material, tetrachloromethane, tetrafluoromethane, chlorine, trichloromonofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, etc. can be used.

[0076]<Surface coating of a negative electrode> The lithium metal which penetrates a lithium ion selectively and deposits a negative electrode surface of a cell of this invention can heighten further depressor effect of dendrite generating at the time of charge by covering with a coat of an insulator film which is not penetrated or semiconductor membrane.

[0077]As a material which covers a negative electrode surface of this invention, what has fine pores or molecular structure which can penetrate a lithium ion is used. Polymers which have the structure of having structure of large coronary ether, carixarene (ring compound of the shape of a cup which comprises two or more phenol units), and an ether bond etc., as an example of a thing which has the molecular structure which can penetrate a lithium ion are mentioned. A vitrified substance etc. which a lithium ion intercalates can be used for others. As a method of producing positively fine pores which can penetrate a lithium ion, into coating liquid of a film material, a foaming agent or material which carries out a pyrolysis easily etc. which mixes material in which elution after coat formation of electrolyte salt etc. is possible is mixed, and a method of producing fine pores can be adopted.

[0078]<In-and-out power terminal of a negative electrode> An in-and-out power terminal of a negative electrode is pulled out from a collecting section which arranges a metallic element which does not make lithium and an alloy of a negative electrode. The technique of connecting a member of a conductor to a collecting section by methods, such as laser welding, spot welding, and solder connection, is used for a drawer of a terminal. When a negative electrode which makes a subject a metallic element which makes lithium and an alloy on it by using as a charge collector a substrate which comprises a metallic element which does not make lithium and an alloy is formed, a

drawer part beforehand connected to an in-and-out power terminal may be processed and provided in a charge collector.

[0079]A lithium secondary battery anode anode comprises a charge collector, positive active material, an electric conduction adjuvant, a binder, etc., mixes positive active material, an electric conduction adjuvant, a binder, etc., and fabricates and produces them on a charge collector. Carbon powder and carbon fiber, such as powder state or fibrous aluminum, copper, nickel, a stainless steel, carbon black, Ketchen black, and acetylene black, can be used for an electric conduction adjuvant used for an anode. As a binder, a stable thing is preferred to an electrolysis solution, for example, polytetrafluoroethylene, poly fluoridation kinky thread NIDEN, polyethylene, polypropylene, an ethylene propylene copolymer, an ethylene-propylene-diene terpolymer, etc. are mentioned to it.

[0080]A charge collector is bearing a duty which collects current which supplies current consumed efficiently or is generated in an electrode reaction at the time of charge and discharge. Therefore, construction material [inertness / cell reaction] whose electric conductivity is high is desirable. As desirable construction material, nickel, titanium, copper, aluminum, a stainless steel, platinum, palladium, gold, zinc, various alloys, and two or more sorts of composite metals of the above-mentioned material are mentioned. As shape of a charge collector, shape, such as tabular, foil form, mesh state, the shape of sponge, fibrous, a punching metal, and an expanded metal, is employable.

[0081]As for positive active material, generally, a transition metal oxide and transition metal sulfide are used. As a transition metal element of a transition metal oxide or transition metal sulfide, By an element which has d husks or f husks selectively, Sc, Y, a lanthanoids, actinoid, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, Pt, Cu, Ag, and Au are used. It is mainly preferred to use Ti of the first sere metal, V, Cr, Mn, Fe, Co, nickel, and Cu.

[0082]It is more desirable to use for the above-mentioned positive active material what contains lithium in a transition metal oxide or transition metal sulfide. Since a negative electrode which contained lithium beforehand by using an anode which comprises positive active material containing lithium is not prepared, there is an advantage which can do a manufacturing process of a cell simple. A salt of lithium hydroxide or lithium is used for one of the preparing methods of positive active material containing lithium, and a method of preparing a transition metal oxide and transition metal sulfide can be used for it. There is also a method of mixing, heat-treating and preparing lithium compounds which are easy to cause a thermal decomposition reaction, such as lithium hydroxide, a lithium nitrate, and lithium carbonate, to a transition metal oxide or transition metal sulfide as other methods.

[0083]A separator separator is arranged between a negative electrode and an anode, and has a role which prevents a short circuit of a negative electrode and an anode. It may have a duty holding an electrolysis solution. SEPARETA has fine pores which a lithium

ion can move, and since it needs to be insoluble to an electrolysis solution, and stable, a thing of material of nonwoven fabrics, such as glass, polypropylene, polyethylene, a fluoro-resin, and polyamide, or micropore structure is used. A resin film which composite-ized a metallic-oxide film or a metallic oxide which has micropore can also be used. When a metallic-oxide film which has especially multilayer-like structure is used, prevention from a short circuit has an effect that it is hard to penetrate a dendrite. When glass and a metallic-oxide film which are a fluoro resin film or an incombustible material which is a fire retarding material are used, safety can be improved more.

[0084]An electrolyte electrolyte uses what added and fixed gelling agents, such as polymer, in a solution and a solution which dissolved in a solvent else [in a case of using it in the state as it is]. Generally, it is used for it, making a solvent carry out liquid retaining of the electrolysis solution which melted an electrolyte to a porous separator.

[0085]As electrolytic conductivity is high, it is desirable, and at least, a certain thing of conductivity in 25 ** is [more than $1x10^{-3}$S/cm] desirable, and a certain thing is [more than $5x10^{-3}$S/cm] more preferred [conductivity].

[0086]An electrolyte Acid, such as H_2SO_4, HCl, and HNO_3, Salts which comprise a lithium ion (Li^+) and Lewis acid ion (BF^{4-}, PF^{6-}, ClO^{4-}, CF_3SO^{3-}, BPh^{4-} (Ph: phenyl group)), and such mixed salt can be used. Besides the above-mentioned supporting electrolyte, a salt of positive ions, such as sodium ion, potassium ion, and tetra alkylammonium ion, and Lewis acid ion can also be used. As for the above-mentioned salt, it is desirable to heat under decompression and to perform sufficient drying and deoxidization.

[0087]As an electrolytic solvent, acetonitrile, benzonitrile, propylene carbonate, Ethylene carbonate, dimethyl carbonate, diethyl carbonate, Dimethylformamide, a tetrahydrofuran, nitrobenzene, a dichloroethane, Diethoxyethane, 1,2-dimethoxyethane, chlorobenzene, gamma-butyrolactone, Dioxolane, sulfolane, nitromethane, dimethyl sulfide, Dimethyl ape oxide, dimethoxyethane, methyl formate, 3-methyl-2-OKIDAZORIJINON, 2-methyltetrahydrofuran, 3-propyl sydnone, sulfur dioxide, a phosphoryl chloride, a thionyl chloride, a sulfuric chloride, etc. can use these mixed liquor.

[0088]It may dry with activated alumina, a molecular sieve, diphosphorus pentaoxide, a calcium chloride, etc., or the above-mentioned solvent may be distilled under alkaline metal coexistence in inactive gas depending on a solvent, and may also perform impurity removal and drying.

[0089]Gelling is preferred in order to prevent disclosure of an electrolysis solution. It is desirable to use polymer which absorbs a solvent of an electrolysis solution and swells as a gelling agent, and polymer, such as polyethylene oxide, polyvinyl alcohol, polyacrylamide, is used.

[0090]shape of a cell, and structure -- shape of a actual cell does not have restrictions in particular, and there are cells, such as a flat type, cylindrical, the Naokata form type, a

sheet type. In spiral type cylindrical, on both sides of a separator, an electrode area can be enlarged by ****** between a negative electrode and an anode, and a high current can be sent at the time of charge and discharge. In a rectangular parallelepiped type, storage space of apparatus which stores a rechargeable battery can be used effectively. Structures, such as a monolayer type and a multilayer type, can be used also as a structure.

[0091]Drawing 4 and drawing 5 are examples of an outline sectional view of a monolayer type flat cell and a spiral structure cylindrical cell, respectively. In drawing 4 and drawing 5, a negative pole collector, and 301 and 401 300 and 400 Negative electrode active material, 303 and 403 -- positive active material and 404 -- a positive pole collector, and 305 and 405 -- a negative pole terminal (negative-electrode cap), and 306 and 406 -- a positive electrode can, and 307 and 407 -- an electrolyte, a separator, and 310 and 410 -- insulating packing and 411 -- an electric insulating plate -- it comes out.

[0092]After including in the positive electrode can 306,406 on both sides of the separator 307,407 as an example of an assembly of a cell of drawing 4 or drawing 5 with the negative electrode active material 301,401 and the fabricated positive active material 303,403 and pouring in an electrolyte, The negative-electrode cap 305,405 and the insulating packing 310,410 are constructed, and caulking ****** is produced. The negative pole collector 300,400 in a figure is connected to metal which does not make lithium and an alloy of the quality 301,401 of negative electrode active material as shown in drawing 2 and drawing 3. Negative pole collector 300,400 itself may be considering it as metal which does not make lithium and an alloy depending on the case.

[0093]As for preparation of material of a lithium cell, and an assembly of a cell, it is desirable for moisture to carry out in dry air removed enough or dry inactive gas.

[0094]As a material of the insulating packing insulating packing 310,410, a fluoro-resin, polyamide resin, polysulfone resin, and various rubbers can be used. It can be closed whether as the obturation method, gaskets, such as insulating packing, were used like drawing 4 and drawing 5, and methods, such as the glass sealed tube, adhesives, welding, and soldering, can be conveniently used also for except.

[0095]As a material of the electric insulating plate 411 of drawing 5, various organic resin materials and ceramics can be used conveniently.

[0096]an outer can -- as the positive electrode can 306,406 of a actual cell, or a material of the negative-electrode cap 305,405, a stainless steel especially titanium clad stainless steel and copper clad stainless steel, a nickel plate steel plate, etc. can be used conveniently.

[0097]Although the positive electrode can 306,406 serves as a cell case in drawing 4 and drawing 5, as construction material of a cell case, composite of plastics, such as metal, such as zinc, and polypropylene, or metal, glass fiber and a plastic can be used besides a stainless steel.

[0098]Although not illustrated by safety valve drawing 4 and drawing 5, as edfety when internal pressure of a cell increases, it is preferred that safety valves, such as rubber, a spring, a metal ball, and burst foil, provide.

[0099]

[Example]Hereafter, based on an example, this invention is explained in detail. This invention is not limited to these examples.

[0100](Example 1) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4. After dipping 50%-50% ground in thickness of 50 microns of titanium aluminum alloy foil for 5 minutes in 5wt% of the potassium hydroxide solution and etching surface aluminum, rinsing desiccation was carried out and it was used as the negative electrode 301 (metallic element with which titanium does not build lithium and an alloy). By the surface polish and etching process of the titanium aluminum alloy plate before production of the above-mentioned negative electrode, it adjusted so that the surface roughness measured with the stylus method of an anode and the negative electrode surface which counters would be 0.6 micron or less by arithmetical mean deviation of profile and might be 3.8 microns or less with the maximum height. At this time, the number of the mountains of roughness was 7 to the measurement length of 80 microns.

[0101]As positive active material, after mixing electrolytic manganese dioxide and lithium carbonate by the ratio of 1:0.4, it heated at 800 ** and the lithium manganic acid ghost was prepared. After having mixed carbon powder 3 weight [of acetylene black] (wt) %, and poly fluoridation kinky thread NIDEN powder 5wt% to the prepared lithium manganic acid ghost, adding N-methyl-2-pyrrolidone and preparing to paste state, spreading desiccation was carried out and the anode was formed in aluminium foil.

[0102]What carried out 1M (mol/l) dissolution of the tetrafluoride lithium borate salt was used for the equivalent mixed solvent of ethylene carbonate (EC) and JIMETOKI carbon NETO (DMC) from which moisture was fully removed at the electrolysis solution.

[0103]The separator sandwiched the nonwoven fabric and micropore film made from polypropylene, and what was adjusted to a thickness of 50 microns was used for it.

[0104]Perform an assembly in dry argon gas atmosphere, insert a separator between a negative electrode and an anode, and it inserts in the positive electrode can of the stainless material of a titanium clad, After pouring in an electrolysis solution, it sealed with the negative-electrode cap of the stainless material of a titanium clad, and the insulating packing of fluorocarbon rubber, and the lithium secondary battery was produced.

[0105](Example 2) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0106]First, the negative electrode was produced in the following procedures. Washing desiccation was carried out, after dipping the aluminium foil of 30-micron thickness in

5% of potassium hydroxide solution for 5 minutes and etching the surface. Subsequently, it dipped for 5 minutes in 20wt% of 50 ** nickel chloride solution, after nickel replaced a part of aluminum of both the surfaces, it rinsed, and reduced pressure drying was carried out at 150 ** (metallic element with which nickel does not build lithium and an alloy). By the surface polish and the etching process, it adjusted so that the surface roughness measured with the stylus method of an anode and the negative electrode surface which counters would be 0.4 micron or less by arithmetical mean deviation of profile and might be 2.0 microns or less with the maximum height. At this time, the number of the mountains of roughness was 8 to the measurement length of 80 microns.

[0107]The 25-micron-thick micropore film made from polypropylene was used for the separator.

[0108]The following assembled the cell like Example 1.

[0109](Example 3) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 6.

[0110]Into the glass-transition-temperature-30 ** epoxy resin, the conductive ink which distributed silver pulverized coal was formed by a thickness of 10 microns by screen-stencil, bridge construction hardening was carried out at 150 ** under decompression, the conductive layer was formed in the field by the side of current collection of the negative electrode produced by the same operation as Example 2, and the negative electrode was produced.

[0111]The following assembled the cell like Example 1.

[0112](Example 4) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0113]First, the negative electrode was produced in the following procedures. Washing desiccation was carried out, after dipping the aluminium foil of 30-micron thickness in 5% of hydrofluoric acid solution and etching the surface. Subsequently, 50-nanometer-thick coppering is performed to both the surfaces in the mixed water solution of copper sulfate and sulfuric acid, After carrying out reduced pressure drying at 150 **, the SUZU bismuth alloy was formed in the field by the side of current collection by a thickness of 500 nanometers by sputtering, and the negative electrode was produced (the metallic element from which copper does not make lithium and an alloy, the alloy in which a ****- bismuth alloy forms a conductor layer with a high pace of expansion). By the surface polish and the etching process, it adjusted so that the surface roughness measured with the stylus method of an anode and the negative electrode surface which counters would be 0.3 micron or less by arithmetical mean deviation of profile and might be 1.7 microns or less with the maximum height. At this time, the number of the mountains of roughness was 8 to the measurement length of 80 microns.

[0114]The following assembled the cell like Example 1.

[0115](Example 5) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0116]First, the negative electrode was produced in the following procedures. aluminium powder [of 300 meshes]: -- poly fluoridation kinky thread NIDEN powder [of a binder]: -- acetylene black: -- flake-like black lead by the weight ratio of 89:5:3:3, [mix and] N-methyl-2-pyrrolidone was added, the paste was prepared, it applied to tinning copper foil of 35-micron thickness, coating thickness was uniformly adjusted with the roll press machine, reduced pressure drying was carried out at 150 **, and the negative electrode of 70-micron thickness was produced.

[0117]The following assembled the cell like Example 1.

[0118](Example 6) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0119]First, the negative electrode was produced in the following procedures. In the punching metal foil of the iron which carried out the nickel plate, the methyl cellulose of the nickel superfines:binder with an aluminium powder:particle diameter of 0.1 micron or less of 300 meshes is mixed by the weight ratio of 90:5:5, Xylene was added, and it was made paste state, and applied to the nickel foil of 35-micron thickness by the coating machine, coating thickness was uniformly adjusted with the roll press machine, and it dried at 100 **. Subsequently, it was made to sinter under decompression of 700 **.

[0120]Next, 50 ** was immersed in 20wt% nickel chloride solution for 5 minutes, substitution processing of a part of aluminum of aluminium powder was carried out with nickel, after washing desiccation, reduced pressure drying was carried out at 150 **, and the negative electrode of 60-micron thickness was produced.

[0121]The following assembled the cell like Example 1.

[0122](Example 7) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0123]First, the xylene solution of the copolymer (trade name sault PAKO nak F) of the Nippon Oil & Fats tetrafluoroethylene and vinyl ether and the dimethyl carbonate solution of lithium borofluoride were mixed, and the solution for surface coating was prepared. in addition -- as opposed to the whole solution which mixed lithium borofluoride -- 1wt% -- it mixed. Next, the anode of the negative electrode produced by the same operation as Example 4 and the solution for surface coating previously prepared by the spinner on the surface which counters were applied, dry hardening was carried out at 170 ** under decompression, it irradiated with ultraviolet rays further, and the negative electrode which carried out surface coating of the lithium ion permeable membranes of about 100 nanometers of thickness was produced.

[0124]The following assembled the cell like Example 1.

[0125]In order to evaluate the performance of a negative electrode to the positive active material of the above-mentioned Examples 1-9, one kind of lithium manganic acid

ghost was used, but it is not limited to this and various kinds of positive active material, such as a lithium nickel oxide and a lithium cobalt oxide, can also be adopted.

[0126]Although the thing same to Examples 1-9 was used also about the electrolysis solution, this invention is not limited to this.

[0127](Comparative example 1) The cell of the outline section structure which was changed to the negative electrode of Example 1 and shown in drawing 4 like the example using the aluminium foil of 30-micron thickness was produced in the same procedure as Example 1. The surface roughness measured with the stylus method of an anode and the negative electrode surface which counters was 0.7 micron or less in 0.15 micron or less and the maximum height at arithmetical mean deviation of profile. At this time, the number of the mountains of roughness was 6 to the measurement length of 80 microns.

[0128](Comparative example 2) 100 which changed to the negative electrode of Example 1 and carried out the etching process of the Japan Capacitor Industrial surface.

[0129]First, the negative electrode was produced in the following procedures. Nickel aluminum alloy powder of 40%-60% of 250 meshes : The methyl cellulose of a binder is mixed by the weight ratio of 90:10, Xylene was added, and it was made paste state, and applied to the expanded metal foil of nickel of 35-micron thickness by the coating machine, coating thickness was uniformly adjusted with the roll press machine, and it dried at 100 **. Subsequently, it was made to sinter under decompression of 700 **. Next, it was immersed in 5wt% of the potassium hydroxide solution for 5 minutes, the etching process of the surface was carried out, and the negative electrode of 50-micron thickness was produced.

[0130]The following assembled the cell like Example 1.

[0131](Example 8) Structure and an assembly produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0132]First, the negative electrode was produced in the following procedures. lithium aluminum-alloy-powder [of 50%-50% of 300 meshes]: -- magnesium powder [of 150 meshes]: -- the acetyl cellulose of a binder by the weight ratio of 45:45:10, [mix and] Xylene was added, and it was made paste state, and applied to the expanded metal foil of nickel of 35-micron thickness by the coating machine, coating thickness was uniformly adjusted with the roll press machine, and it dried at 100 **. Subsequently, it was made to sinter under decompression of 700 **. Next, it was immersed in 5wt% of the potassium hydroxide solution for 5 minutes, the etching process of the surface was carried out, and the negative electrode of 60-micron thickness was produced.

[0133]The following assembled the cell like Example 1.

[0134](Example 9) Structure and an assembly produced the cell of the outline section structure shown in drawing 4 like the example in the same procedure as Example 1 using the aluminium foil of the micron thickness which produced the lithium secondary battery of the outline section structure shown in easy drawing 4.

[0135](Comparative example 3) The cell of **** for graphite negative electrodes which was changed to the negative electrode of Example 2 and produced in the following procedures, and the outline section structure shown in drawing 4 like the example was produced in the same procedure as Example 2. After a graphite negative electrode heat-treats natural graphite powder at 2000 ** under argon gas, natural graphite powder: -- acetylene black: -- poly fluoridation kinky thread NIDEN powder by the weight ratio of 82:3:5, [mix and] After adding N-methyl-2-pyrrolidone and preparing to paste state, it applied to copper foil of 35-micron thickness, coating thickness was uniformly adjusted with the roll press machine, reduced pressure drying was carried out at 150 **, and the negative electrode of 110-micron thickness was produced.

[0136]The charge-and-discharge cycle test was done for the quality assessment of the lithium secondary battery produced by the quality assessment example and comparative example of the lithium secondary battery on condition of the following, and the performance was evaluated as compared with the cell of a comparative example.

[0137]The conditions of the cycle test were made into the recess for cut-off voltage 4.5 V or 30 minutes of the charge and discharge of 0.5C (0.5 time as much current as capacity/time), and charge, and the cut-off voltage 2.5V of discharge on the basis of the electric capacity calculated from cathode active material volume. The cut-off voltage of charge decided that disassembly of the solvent in an electrolysis solution was not advanced. Hokuto Denko HJ-106M was used for the charging and discharging device of a cell. The charge and discharge test was started from charge, cell capacity was made into the 3rd discharging amount, and the cycle life was made into the number of times of a cycle to which charging potential amounted to 4.5V.

[0138]The performance (service capacity and cycle life) of the cell of the comparative example 1 was standardized as 1.0, and the evaluation result of the performance about the spark discharge energy density and the cycle life of the lithium cell produced using the negative electrode of this invention, i.e., the cell of an example and a comparative example, per unit volume was collectively shown in Table 1.

[0139]By adopting the rechargeable battery using the negative electrode of this invention, making a negative electrode surface into activity from comparison of Examples 1-9 and the comparative examples 1 and 2, so that he can understand from Table 1, and raising current collection ability showed that a cycle life was extended. Comparison of Examples 1-9 and the comparative example 3 showed that a rechargeable battery with a high energy density was producible, although the life was almost the same compared with the carbon negative electrode.

[0140]

[Table 1]

表　1

	エネルギー密度	サイクル寿命
実施例１の二次電池	1.4	2.9
実施例２の二次電池	1.6	3.2
実施例３の二次電池	1.5	3.7
実施例４の二次電池	1.6	3.5
実施例５の二次電池	1.3	3.3
実施例６の二次電池	1.4	3.6
実施例７の二次電池	1.4	3.4
実施例８の二次電池	1.4	3.6
実施例９の二次電池	1.6	3.9
比較例１の二次電池	1.0	1.0
比較例２の二次電池	1.1	1.3
比較例３の二次電池	1.0	4.2

[0141]
[Effect of the Invention]According to above-mentioned this invention, the lithium secondary battery of high energy density with a long charge-and-discharge cycle life can be provided.
[0142]According to this invention, the lithium secondary battery which has the electrode for cells and this electrode which have the negative electrode structure which can suppress the fall of the current collection ability by the pulverization by the deposit dissolution of lithium and crack initiation at the time of charge and discharge can be provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a notional lineblock diagram for explaining a suitable example of the rechargeable battery of this invention.
[Drawing 2](a), (b), (c), and (c') are the typical sectional views for explaining a suitable example of the negative electrode of this invention, respectively.
[Drawing 3](d), (e), (f), and (g) are the typical sectional views for explaining a suitable

example of the negative electrode of this invention, respectively.

[Drawing 4]It is an outline sectional view for explaining an example of a monolayer type flat cell.

[Drawing 5]It is an outline sectional view for explaining an example of a spiral structure cylindrical cell.

[Drawing 6]It is a figure for explaining an example of the measurement result of the negative electrode surface by a stylus method.

[Drawing 7]It is a figure showing an example of the relation between the difference of one half and arithmetical-mean-deviation-of-profile Ra of maximum height Rmax of the surface roughness of the conductor portion of a negative electrode surface, and the cycle life of a negative electrode.

[Drawing 8]It is a figure showing an example of the relation between several n of the mountain of per the measurement length [arithmetical-mean-deviation-of-profile Ra of the conductor portion of a negative electrode surface, the measurement length L, and] L, and the cycle life of a negative electrode.

[Description of Notations]

101 The collecting section which comprises the metallic element which does not make lithium and an alloy

102 The member containing the metallic element which makes lithium and an alloy

103 The powder state member containing the metallic element which makes lithium and an alloy

104 Electric conduction adjuvant

105 Binder

106 The metallic element which does not make lithium and an alloy

107 A conductive layer with a high pace of expansion

108 The alloy of the metallic element which does not make the metallic element and lithium which make lithium and an alloy, and an alloy

200 Collecting section

201 The layer which consists of a member containing the metallic element which makes lithium and an alloy

202 Negative electrode

203 Anode

204 Electrolyte (electrolysis solution)

205 Separator

206 Negative pole terminal

207 Positive pole terminal

208 Cell case

300 Negative pole collector

301 Negative electrode active material (or negative electrode)

303 Positive active material (or anode)

305 Negative pole terminal
306 Positive electrode can
307 An electrolyte and a separator
310 Insulating packing
400 Negative pole collector
401 Negative electrode active material (or negative electrode)
403 Positive active material (or anode)
404 Positive pole collector
405 Negative pole terminal
406 Positive electrode can
407 An electrolyte and a separator
410 Insulating packing
411 Electric insulating plate